(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 June 2001 (21.06.2001)

PCT

(10) International Publication Number
WO 01/44561 A1

(51) International Patent Classification[7]: D06L 1/16, C11D 7/14, 7/10

(21) International Application Number: PCT/EP00/11563

(22) International Filing Date: 17 November 2000 (17.11.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
9929838.2 16 December 1999 (16.12.1999) GB

(71) Applicant *(for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, TZ, UG, ZA, ZW only)*: **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant *(for all designated States except AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, IN, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, TZ, UG, US, ZA, ZW)*: **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant *(for IN only)*: **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **BIRD, Nigel, Peter** [GB/GB]; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **HOWELL, Ian** [GB/GB]; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **MARR, Abigail** [GB/GB]; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). **YORKE, John, William, Harol** [GB/GB]; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).

(74) Agents: **FRANSELLA, Mary, Evelyn** et al.; Unilever PLC, Patent Dept., Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 01/44561 A1

(54) Title: PROCESS AND COMPOSITION FOR LAUNDERING OF TEXTILE FABRICS

(57) Abstract: A process for the laundering of textile fabrics, which comprises: (i) a wash step in which the fabrics are immersed in an aqueous wash liquor comprising a detergent surfactant, a detergency builder and optionally other detergent ingredients; (ii) a rinse step in which the fabrics are immersed for at least 30 seconds in an aqueous rinse liquor comprising (a) at least 0.02 g/l of a light coloured crystalline clay mineral, and optionally a non-surfactant water-soluble salt. A composition suitable for use in this process comprises: (a) from 2 to 98 wt% of a light coloured crystalline clay mineral; and (b) from 98 to 2 wt% of a non-surfactant water-soluble inorganic salt, the weight ratio of (a):(b) being from 49:1 to 1:49, and is substantially free of synthetic non-soap surfactant.

# PROCESS AND COMPOSITION FOR LAUNDERING OF TEXTILE FABRICS

## Field of the Invention

The present invention relates to a process and a composition for the laundering of textile fabrics.

## Background of the Invention

In countries where textile fabrics are habitually washed by hand, even using premium products, the degree of cleaning achieved is frequently disappointing.

One obvious route to improving handwash performance is to try to improve the ingredients in the main wash detergent formulation. However, the present inventors have now discovered that cleaning performance can be significantly enhanced by including a clay in the rinse liquor.

Without being bound by any theory or explanation, the inventors have conjectured that the clay exerts its effect by remaining on the clothes after they have dried and acts as a sacrificial layer, to which dirt adheres and so is more easily removed during subsequent washing the next time. This avoids a build-up of particulate soil on the fabric.

Pelletised compositions comprising, *inter alia*, smectite clay and magnesium sulphate for fibre softening use, are disclosed in JP-A-10 331066 and JP-A-10 331067.

A fabric softening composition which may be used in the rinse cycle, containing a fabric softening bentonite clay and an isostearamide antistatic agent is disclosed in GB-A-2 170 236. Exemplified compositions contian surfactant.

Other compositions containing clay, water soluble non-surfactant salt (electrolyte) and surfactant, are disclosed in GB-A-2 207 144, GB-A-2 170 236, GB-A-1 303 810, EP-A-0 947 203, EP-A-0 146 289, EP-A-0 139 330 and EP-A-0 026 529.

Definition of the Invention

Thus, a first aspect of the present invention provides a process for the laundering of textile fabrics, which comprises:

(i) a wash step in which the fabrics are immersed in an aqueous wash liquor comprising a detergent surfactant, a detergency builder and optionally other detergent ingredients; and

(ii) a rinse step in which the fabrics are immersed for at least 30 seconds in an aqueous rinse liquor comprising;

(a) at least 0.02 g/l, preferably at least 0.1g/l of a light coloured crystalline clay mineral; and

(b) a non-surfactant water-soluble salt.

A second aspect of the present invention provides a composition for treating laundered textile fabrics in the rinse, which comprises: (a) from 2 to 98 wt% of a light coloured crystalline clay mineral; and (b) from 98 to 2 wt% of a water-soluble inorganic salt, the weight ratio of (a):(b) being from 49:1 to 1:49, preferably from 20:1 to 1:2, more preferably from 10:1 to 1:2, and the composition being substantially free of non-soap surfactant.

Detailed Description of the Invention

The present invention exerts its beneficial effect by incorporation of a light coloured crystalline clay material in the rinse liquor, also with a non-surfactant water-soluble salt. Optionally, there may be more than one rinse but at least one rinse must conform with rinse step (ii) according to the present invention. Preferably also, the rinse liquor in step (ii) is substantially free of detergent. For example, the rinse liquor in step (ii) preferably contains < 0.25g/l, more preferably < 0.1g/l, most preferably <0.05g/l of synthetic non-soap surfactant and most preferably is completely devoid of such surfactant.

**A. The Wash Step (i)**

The wash step (i) utilises an aqueous wash liquor comprising detergent surfactant, detergency builder and optionally, other ingredients. This will normally be formed from dissolving a detergent wash product containing these ingredients.

Detergent Surfactants

The composition of a suitable wash product typically comprises one or more deterging synthetic non-soap surfactants, chosen from anionic, nonionic, cationic and zwitterionic surfactants and mixtures thereof, as will be well known to those skilled in the art. Soap may also be included in the composition. Many suitable surface-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and non-ionic compounds.

The compositions of the wash product may for example contain linear alkylbenzene sulphonate, particularly linear alkylbenzene sulphonates having an alkyl chain length of

$C_8$-$C_{15}$. It is preferred if the level of linear alkylbenzene sulphonate is from 0 wt% to 30 wt%, more preferably 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt%.

The compositions of the wash product may contain other anionic surfactants in amounts additional to the percentages quoted above. Suitable anionic surfactants are well-known to those skilled in the art. Examples include primary and secondary alkyl sulphates, particularly $C_8$-$C_{15}$ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

The compositions of the wash product may also contain non-ionic surfactant. Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the $C_8$-$C_{20}$ aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the $C_{10}$-$C_{15}$ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

It is preferred if the level of non-ionic surfactant is from 0 wt% to 30 wt%, preferably from 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt%.

It is also possible to include certain mono-alkyl cationic surfactants which can be used in main-wash compositions for fabrics. Cationic surfactants that may be used include quaternary ammonium salts of the general formula $R_1R_2R_3R_4N^+ X^-$ wherein the R groups are long or short hydrocarbon chains, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a counter-ion (for example, compounds in which $R_1$ is a $C_8$-$C_{22}$ alkyl group, preferably a $C_8$-$C_{10}$ or $C_{12}$-$C_{14}$ alkyl group, $R_2$ is a methyl group, and $R_3$ and $R_4$, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters).

The choice of surface-active compound (surfactant), and the amount present, will depend on the intended use of the detergent composition. In fabric washing compositions, different surfactant systems may be chosen, as is well known to the

skilled formulator, for handwashing products and for products intended for use in different types of washing machine.

The total amount of surfactant present will also depend on the intended end use and may be as high as 60 wt%, for example, in a composition for washing fabrics by hand. In compositions for machine washing of fabrics, an amount of from 5 to 40 wt% is generally appropriate. Typically the compositions will comprise at least 2 wt% surfactant e.g. 2-60%, preferably 15-40% most preferably 25-35%.

Detergent compositions suitable for use in most automatic fabric washing machines generally contain anionic non-soap surfactant, or non-ionic surfactant, or combinations of the two in any suitable ratio, optionally together with soap.

Builders

The compositions of the main wash product also contain one or more detergency builders.

The total amount of detergency builder in the wash compositions will typically range from 5 to 80 wt%, preferably from 10 to 60 wt%.

Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever); crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514B (Hoechst). Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate are also suitable for use with this invention.

The compositions of the wash product preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula: 0.8-1.5 $Na_2O$. $Al_2O_3$. 0.8-6 $SiO_2$

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 $SiO_2$ units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

Optionally, organic builders such as citrates, suitable used in amounts of from 5 to 30 wt%, preferably from 10 to 5 wt% are used.

Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

**B. The Rinse Step (ii)**

Compositions according to the second aspect of the present invention are substantially free of synthetic non-soap surfactant, for example containing less than 10%, preferably less than 5%, more preferably less than 1%, especially less than 1% or substantially zero% by weight of the composition of such surfactant. Typical use concentrations are from 1 to 5, e.g. 2.5 grams/litre of water.

The Clay

Compositions according to the present invention contain from 2 to 98 % by weight of a light coloured crystalline clay material, so as to be suitable for yielding preferably at least 0.02 g/l, more preferably at least 0.1 g/l of the clay in the rinse liquor, and preferably no more than 30g/l.

Preferably, crystalline clay mineral is selected from one or more clays selected from one or more clays selected from bi-layer clays, e.g. china clay and halloysite, dioctahedral clays such as kaolinite, trioctahedral clays such as antigorite and amesite, smectite and hormite clays such as bentonite (montmorillonite), beidelite, nontronite, hectorite, attapulgite, pimelite, mica, muscovite and vermiculite clays, as well as pyrophyllite/talc, willemseite and minnesotaite clays.

The crystalline clay mineral must be light coloured. Preferably, it should have a reflectance of at least 60, more preferably at least 70, especially at least 80 at a wavelength of 460 nm. Preferably also, the number average particle diameter of the clay mineral particles should not exceed 2μm, especially not exceeding 1μm. This particle size diameter is that obtained measured by use of a Malvern Zetasizer™ , using a dispersion of the clay mineral at 0.1 g/l in deionised water at 25°C, the clay being dispersed by vigorous hand agitation using a glass rod stirrer for 1 minute.

Optional Water-soluble Salt

The optional water-soluble salt is believed to be beneficial because it promotes dispersion and assists flocculation of the clay particles in the rinse liquor and enables them to be uniformly dispersed in so deposit more uniformly on the fabric.

Any non-surfactant water-soluble salt may be used. The term "non-surfactant" salt is used because many surfactants, e.g. anionic surfactants are in the form of water soluble alkali metal salts and cationic surfactants are usually in water-soluble salt form with a counter-anion. For the non-surfactant water-soluble salts, salts of the metal cations with inorganic or organic anions are appropriate. A mixture of salts may also be used, but it is preferable to use a material which is widely available at low cost. Thus, one may use a soluble salt of a monovalent metal such as an alkali metal, for example sodium or potassium, e.g. as the chloride or sulphate. However, weight for weight, it is more effective to use a salt of a divalent metal, or a water-soluble salt of a metal having a valency of three or more. It could also be a water-soluble detergency builder such as an alkali metal citrate or tripolyphosphate. However, the best balance of cheapness and effectiveness has been found to be obtained if the salt comprises magnesium ions. Magnesium chloride and/or sulphate are typical. The amount of salt used will depend on the valency of the metal but in the broadest concept, it will be used at a molar concentration of from 0.001M to 1M. In the case of the magnesium salt, the molar concentration will usually be from 0.001M to 0.1M in the rinse liquor. Thus, in the compositions according to the present invention, the amount of the water-soluble inorganic salt will be from 2-98 % by weight of the composition and in particular, for a magnesium chloride and/or sulphate, from 5 to 70 % by weight.

Other Optional Ingredients

Compositions of the present invention optionally may contain one or more additional benefit agents for subsequent dispersion and/or solution in the wash step (i) and/or in the rinse liquor of step (ii). These may, for example, be selected from fluorescers,

perfumes, starches, enzymes such as lipases, soil-release polymers, photobleaches and blueing agents. However, as already stated, the composition, and therefore the rinse liquor, is preferably substantially free from organic surfactant. Detergency builders may also be included. Those which are water-soluble salts will form all or part of the water-soluble salt (b) if used in rinse step (ii).

Any fluorescer present is preferably incorporated in an amount of from 0.01 to 1% by weight of the composition, although the upper limit of this range is more preferably, 0.75%, still more preferably 0.5%, most preferably 0.1% by weight of the composition. Typical perfume levels are from 0.1% to 1%, e.g. from 0.2% to 0.5% by weight of the composition.

Product Form

The compositions of the present invention may be provided in any suitable form to allow convenient dispersion/solution in the rinse liquor by the consumer. Thus, for example, they may be provided as powders or granulated solids. They may also be provided in any of the forms of liquids, pastes, gels, bars or tablets. The compositions may be provided in a product form whereby they are provided alongside a main wash product, for example comprising a detergent surfactant, a detergency builder and optionally, other detergent ingredients. Conveniently, the main wash product and the rinse composition according to the present invention may be provided in respective secondary packaging inside a unitary primary package.

The present invention will now be explained in more detail by reference to the following non-limiting examples.

**General Protocol**

1. Rinse clean fabric in clay plus electrolyte.
2. Expose to soiling by hanging in the air exhaust of a road traffic tunnel for one week.
3. Wash dirty cloths in a commercial laundry wash product (2.5g/l)

**Soiling Method**

The soiling method imitates the environmental soiling conditions experienced in urban smogs. This was achieved by placing samples of fabric, within a purpose built frame and then exposing the frame to conditions within an exhaust chamber of the Mersey Tunnel (George's Dock Building). The samples were subjected to an exposure period of one week.

NB: Cloths used for these different experiments were exposed in the tunnel at different times. The soiling levels on the fabrics thus differ, depending on traffic flows and air flow operating at the time of exposure. In each experiment treated and untreated cloths were exposed at the same time and so can be compared directly.

**Rinse Protocol (Clay Application)**

The application of the clay was carried out during the rinse phase on clean cloths. A generalised procedure is illustrated in the table below. However, conditions were sometimes modified (as stated). After drying, the cloths were exposed to soiling and then washed as detailed below.

| | |
|---|---|
| Wash Model | Handwash |
| Equipment | Tergotometer |
| Water Volume | 1 litre |
| Water Hardness | 24°FH |
| Agitation | 100 rpm |
| Electrolyte | As stated |
| Water Temperature | Ambient (21°C-24°C) |
| Liquor : Cloth | As stated |
| Agitation Time | As stated |
| Drying Procedure | Drying Racks |

**Wash Protocol**

A wash protocol to simulate typical handwash conditions was used. Again this is a generalised procedure and deviations are noted accordingly.

| | |
|---|---|
| Wash Model | Handwash |
| Equipment | Tergotometer |
| Water Volume | 1 litre |
| Water Hardness | 24°FH |
| Agitation | 100 rpm |
| Water Temperature | Ambient (21°C-24°C) |
| Liquor : Cloth | As stated |
| Agitation Time | As stated |
| Drying Procedure | Drying Racks |
| Product Dosage | a commercial washing powder (2.5 g/l) |
| Number of Rinses | 2 x 1 litre (24°FH) |

**Analysis**

The Hunterlab Ultrascan XE was used to determine the reflectance values of the cloths. This data was then input into a SAS statistical analysis programme, which was used to generate the ΔR460*nm LS Mean data, which takes into account the variability of the before wash reading of the cloths. ($\Delta R460^* = R_{aw} - R_{bw}$).

**Results**

**1. Dose Response on Cotton Fabric**

| Clay Concentration (g/l) | Talc (ΔR460*nm) | Kaolinite (ΔR460*nm) | Bentonite (ΔR460*nm) |
|---|---|---|---|
| 0 | 31.54 | 31.54 | 31.54 |
| 0.5 | 33.02 | 31.02 | 35.35 |
| 1 | 33.96 | 35.18 | 39.15 |
| 5 | 37.05 | 40.26 | 41.47 |
| 10 | 36.25 | 37.78 | 44.69 |

- Rinse protocol - Clay (levels as stated above), Electrolyte $MgCl_2$ (0.01M), Agitation 15 mins, L:C 40:1. The clay and electrolyte were dispersed in the Tergotometer by agitation.
- Main wash protocol - commercial laundry wash product (2.5 g/l), Water Hardness 24°FH, Agitation 15 mins, L:C 200:1.

**2. Multicycle Experiments - I**

A multicycle experiment was conducted, the steps involved are summarised below:

1. Clay rinse treatment

2. Expose to Mersey Tunnel for one week.
3. Wash in a commercial laundry wash product (2.5g/l)
4. Repeat steps 1-3.

All experiments were conducted on cotton sheeting, unless otherwise stated.

| Clay Pretreatment (20g/l) before Each Mersey Tunnel Exposure | | | | |
|---|---|---|---|---|
| | Control (R460*nm) | Talc (R460*nm) | Kaolinite (R460*nm) | Bentonite (R460*nm) |
| Week One | 69.6 | 75.9 | 76.5 | 81.7 |
| Week Two | 61.5 | 71.8 | 74.8 | 83.9 |

- Rinse protocol - Clay concentration 20g/l, water-soluble salt $MgCl_2$ (0.01M), Agitation time 15 mins, L:C 40:1.

Main wash protocol - commercial laundry wash product (2.5 g/l), Water Hardness 24°FH, Soak 30 mins, Agitation 15 mins, L:C 40:1.

**3. Multicycle Experiments - II**

A multicycle experiment was conducted, the steps involved are summarised below:

1. Clay rinse treatment.
2. Exposed in a road traffic tunnel for one week.
3. Washed in the commercial laundry wash product (2.5g/l)
4. Repeat steps 2-3.

All experiments were conducted on cotton sheeting, unless otherwise stated.

(a) Effect of Clay Type

| One Clay Pretreatment (5g/l) | | | | |
|---|---|---|---|---|
| | Control (R460*nm) | Talc (R460*nm) | Kaolinite (R460*nm) | Bentonite (R460*nm) |
| Week One | 75.6 | 79.7 | 80.6 | 82.5 |
| Week Two | 71.6 | 74.6 | 76.1 | 78.1 |
| Week Three | 68.5 | 71.6 | 72.7 | 75.9 |
| Week Four | 61.2 | 64.7 | 64.9 | 67.7 |

- Rinse protocol - Clay concentration 5g/l, water-soluble salt $MgCl_2$ (0.01M), Agitation time 15 mins, L:C 40:1.
- Main wash protocol - commercial laundry wash product (2.5g/l), Water Hardness 24°FH, Soak time 30 mins, Agitation time 15 mins, L:C 40:1

(b) Effect of Bentonite on different Fabric Types

| One Clay Pre-Treatment (Gelwhite 20g/l) Reflectance at R460* | | | | | | |
|---|---|---|---|---|---|---|
| | Treated Cotton | Untreated Cotton | Treated Polycotton | Untreated Polycotton | Treated Polyester | Untreated Polyester |
| Week One | 83.9 | 61.6 | 82.4 | 50.9 | 82.4 | 59.2 |
| Week Two | 76.3 | 55.2 | 72.0 | 38.8 | 58.6 | 43.8 |
| Week Three | 76.0 | 55.2 | 70.5 | 39.9 | 59.5 | 44.4 |
| Week Four | 68.5 | 49.5 | 62.3 | 43.7 | 58.5 | 36.6 |

- Rinse protocol - Clay concentration 20g/l, Electrolyte $MgCl_2$ (0.01M), Agitation time 5 mins, L:C 40:1.
- Main wash protocol - commercial laundry wash product (2.5 g/l), Water Hardness 24°FH, Agitation time 15 mins, L:C 500:1.

**Shaker Bath Studies**

Effect of Clay level on cloth on after wash reflectance, using Bentonite clay

0.5 $m^2$ pieces of cotton were agitated by hand in 1L of 0.01M $MgCl_2$ containing clay of different levels (see below) for 5 minutes before being wrung out and dried flat overnight. The amount of clay deposited was measured by ashing the cloth at 750°C for 5 hours and weighing the resulting ash as compared with the initial cloth. All weighings were made on desiccated samples and to 4 figures. The pieces were exposed for 1 week in a road traffic tunnel. They were then washed in 50$cm^3$ water or 1$gl^{-1}$ LAS/0.01M NaCl in shaker bath at 100 rpm and 22°C for 20 minutes. Surfactant wash followed by rinse in demineralised water. Reflectance was measured on Macbeth Coloureye 7000.

| Level of Clay on Cloth (%w/w) | After wash Reflectance (R460*) |
|---|---|
| 0.29 | 57.01 |
| 0.53 | 61.33 |
| 0.64 | 72.92 |
| 1.36 | 75.92 |
| 1.83 | 72.44 |

Effect of Clay in Model Shaker Bath Washes : Reflectance Values

| Wash Condition | Untreated | | Treated with 20g/l Bentonite | |
|---|---|---|---|---|
| Wavelength (nm) | 450 | 730 | 450 | 730 |
| Demineralised water | 32.93 ± 2.64 | 38.10 ± 2.84 | 43.19 ± 2.24 | 48.65 ± 2.35 |
| 1 $gl^{-1}$ LAS 0.01M NaCl | 41.84 ± 2.66 | 47.56 ± 2.64 | 70.32 ± 0.899 | 75.66 ± 0.79 |

**Further exemplification of Effect as Function of Clay Type**

After dipping into IM NaCl with the specified amount of the relevant clay mineral, or none (control), and drying, after-wash reflectance values are as shown in the following table:

| Cotton | After Wash Reflectance R460 | | | |
|---|---|---|---|---|
| Amount | 1 | 5 | 10 | 20 |
| Talc | 70.76 | 73.55 | 75.8 | 79.68 |
| Virgo C | 68.26 | 70.38 | 73.97 | 76.02 |
| Indian A | 69.87 | 73.24 | 74.66 | 77.46 |
| Calcite | 65.57 | 65.92 | 69.67 | 70.62 |
| Gelwhite | 72.16 | 76.59 | 76.68 | 77.73 |
| Control | 68.23 | 62.92 | 62.3 | 64.59 |

| Polycotton | After Wash Reflectance R460 | | | |
|---|---|---|---|---|
| Amount | 1 | 5 | 10 | 20 |
| Talc | 65.17 | 66.03 | 67.41 | 72.92 |
| Virgo C | 67.88 | 66.06 | 63.95 | 69.91 |
| Indian A | 69.76 | 66.76 | 67.98 | 71.73 |
| Calcite | 61.67 | 59.81 | 50.74 | 63.25 |
| Gelwhite | 65.12 | 71.47 | 65.07 | 70.3 |
| Control | 59.48 | 58.07 | 50.62 | 56.71 |

**CLAIMS:**

1. A process for the laundering of textile fabrics, which comprises:

(i) a wash step in which the fabrics are immersed in an aqueous wash liquor comprising a detergent surfactant, a detergency builder and optionally other detergent ingredients; and

(ii) a rinse step in which the fabrics are immersed for at least 30 seconds in an aqueous rinse liquor comprising;

(a) at least 0.02 g/l, preferably at least 0.1 g/l of a light coloured crystalline clay mineral; and

(b) a non-surfactant water-soluble salt.

2. A process as claimed in claim 1, wherein the rinse liquor is substantially free of synthetic non-soap surfactant.

3. A process as claimed in either preceding claim, wherein the light coloured crystalline clay material is selected from one or more clays selected from bi-layer clays, e.g. china clay and halloysite, dioctahedral clays such as kaolinite, trioctahedral clays such as antigorite and amesite, smectite and hormite clays such as bentonite (montmorillonite), beidelite, nontronite, hectorite, attapulgite, pimelite, mica, muscovite and vermiculite clays, as well as pyrophyllite/talc, willemseite and minnesotaite clays.

4. A process as claimed in either preceding claim, wherein the light coloured crystalline clay mixed has a reflectance of at least 60, preferably at least 70, more preferably at least 80 at a wavelength of 460 nm.

5. A process as claimed in any preceding claim, wherein the number average particle size of the light coloured crystalline clay mineral does not exceed 2μm, preferably not exceeding 1μm.

6. A process as claimed in any preceding claim, wherein the non-surfactant salt (b) is present at a molar concentration of from 0.001M to 1M.

7. A process as claimed in any preceding claim, wherein the salt (b) is a magnesium salt and is present at a concentration of from 0.005M to 0.1M.

8. A process as claimed in any preceding claim, wherein the rinse liquor also comprises a benefit agent selected from fluorescers, perfumes, starch, lipase, soil release polymers, photobleaches and blueing agents, builders other than any already constituting the water-soluble salt (b).

9. A process as claimed in any preceding claim, wherein the rinse liquor is substantially free of organic surfactant.

10. A process as claimed in any preceding claim in which more than one rinse is carried out, wherein the rinse step (ii) is the final rinse step.

11. A process as claimed in any preceding claim, wherein the wash step (i) is carried out by hand.

12. A composition for treating laundered textile fabrics in the rinse, which comprises:

(a) from 2 to 98 wt% of a white crystalline clay mineral;

(b) from 98 to 2 wt% of a water-soluble inorganic salt;

the weight ratio of (a):(b) being from 49:1 to 1:49, preferably from 20:1 to 1:2, more preferably 10:1 to 1:2;

said composition being substantially free from synthetic non-soap surfactant.

13. A composition as claimed in claim 12 or claim 13, wherein the salt (b) is a magnesium salt.

14. A composition as claimed in claim 12 or claim 13, which further comprises an effective amount of a benefit agent selected from fluorescers, perfumes, starch, lipase, soil release polymers, photobleaches and blueing agents, builders other than any already constituting the water-soluble salt (b).

15. A composition as claimed in any one of claims 12 to 14, which is in the form of a particulate composition, a liquid, a gel, a paste, a bar or a tablet.

16. A laundry detergent product which comprises:

(i) a first composition which comprises a detergent surfactant, a detergency builder and optionally other detergent ingredients,

(ii) a second composition which is as claimed in any one of claims 12 to 15.

17. A product as claimed in claim 16, wherein the first composition (i) is a particulate laundry detergent composition.

18. A product as claimed in claim 16 or claim 17, wherein the first and second compositions are within separate respective secondary packaging, and the secondary packs packed together within common primary packaging.

# INTERNATIONAL SEARCH REPORT

Internatl. Application No
PCT/EP 00/11563

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D06L1/16 C11D7/14 C11D7/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 4 569 773 A (RAMACHANDRAN PALLASSANA N ET AL) 11 February 1986 (1986-02-11)<br>abstract<br>column 19, line 23 - line 35 | 1-6,9, 11,12, 15-17 |
| A | US 5 234 620 A (BRACE ROGER ET AL)<br>10 August 1993 (1993-08-10)<br>abstract; examples G-I | 1,3-5, 12-17 |
| A | US 4 680 916 A (GINN MARTIN E)<br>21 July 1987 (1987-07-21)<br>abstract; figure 2 | 1,8, 16-18 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 27 April 2001 | 10/05/2001 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Saunders, T |

1

Form PCT/ISA/210 (second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internati. Application No
PCT/EP 00/11563

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
|---|---|---|---|---|
| US 4569773 A | 11-02-1986 | US | 4472287 A | 18-09-1984 |
| | | AT | 387787 B | 10-03-1989 |
| | | AT | 433483 A | 15-08-1988 |
| | | AU | 562831 B | 18-06-1987 |
| | | AU | 2229683 A | 21-06-1984 |
| | | BE | 898433 A | 13-06-1984 |
| | | BR | 8306831 A | 24-07-1984 |
| | | CA | 1212504 A | 14-10-1986 |
| | | CH | 658479 A | 14-11-1986 |
| | | DE | 3344098 A | 14-06-1984 |
| | | DK | 572683 A | 14-06-1984 |
| | | ES | 527957 D | 16-04-1985 |
| | | ES | 8504915 A | 16-07-1985 |
| | | FI | 834552 A,B, | 14-06-1984 |
| | | FR | 2537598 A | 15-06-1984 |
| | | GB | 2132241 A,B | 04-07-1984 |
| | | GR | 78786 A | 02-10-1984 |
| | | IT | 1172372 B | 18-06-1987 |
| | | MX | 158721 A | 03-03-1989 |
| | | NL | 8304288 A | 02-07-1984 |
| | | NO | 834557 A,B, | 14-06-1984 |
| | | NO | 881216 A,B, | 14-06-1984 |
| | | NZ | 206539 A | 21-02-1986 |
| | | PH | 22528 A | 17-10-1988 |
| | | PT | 77814 A,B | 01-01-1984 |
| | | SE | 454517 B | 09-05-1988 |
| | | SE | 8306836 A | 14-06-1984 |
| | | ZA | 8309047 A | 31-07-1985 |
| | | ZW | 26983 A | 28-03-1984 |
| US 5234620 A | 10-08-1993 | AU | 629347 B | 01-10-1992 |
| | | AU | 5606590 A | 06-12-1990 |
| | | BR | 9002614 A | 20-08-1991 |
| | | CA | 2017671 A,C | 02-12-1990 |
| | | DE | 69028657 D | 31-10-1996 |
| | | DE | 69028657 T | 13-02-1997 |
| | | EP | 0401047 A | 05-12-1990 |
| | | ES | 2093014 T | 16-12-1996 |
| | | IN | 171323 A | 19-09-1992 |
| | | JP | 2593953 B | 26-03-1997 |
| | | JP | 3027177 A | 05-02-1991 |
| | | KR | 9410650 B | 24-10-1994 |
| | | NO | 902415 A | 03-12-1990 |
| | | TR | 25084 A | 01-11-1992 |
| | | US | 5102562 A | 07-04-1992 |
| | | ZA | 9004217 A | 26-02-1992 |
| US 4680916 A | 21-07-1987 | US | 4588080 A | 13-05-1986 |